

N65-23682

NASA TT F-9349

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Translation of "O vzaimodeystvii nekotorykh tugoplavkikh  
karbidov s dvuokis'yu tsirkoniya"  
Ogneupory, No 12, pp. 570-575, 1964

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
WASHINGTON APRIL 1965

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ABSTRACT

The high-temperature interaction of  $ZrC$  and  $ZrO_2$  mixtures is studied, and they are found to be most stable at these temperatures, with cermets less stable. Lattice parameters of both are discussed. The properties of the cermets indicate usefulness as structural materials.

The interaction of some refractory carbides and oxides is of some practical interest to a variety of high temperature branches of technology. Therefore, the work in this field was started back in 1950.

There is some published information on the properties of cermets in which the principal components are  $Al_2O_3$  and  $Mo_2C$  (ref. 1) designed for cutting tempered and highly alloyed steels and alloys.

Some cermets of the  $Al_2O_3$ - $TiC$  system have been investigated. They are used as high temperature resistance elements (ref. 2). It has been shown that the composition of components does not change significantly and that the properties

\*Numbers given in the margin indicate the pagination in the original foreign text.

of cermets are not additive properties of the starting materials; they are greatly dependent on the ratio of carbide to oxide.

The X-ray diffraction studies of cermets in the MgO-TiC system after high temperature treatment in a vacuum have been carried out and the newly formed phase has been compared with magnesium titanate. A substance was discovered in films on the cooled parts of the furnace which is easily decomposed in air producing acetylene. It was assumed that this is magnesium carbide (ref. 3). Certain properties of the refractory cermets produced by the sintering of carbides of metals of the IV - V groups with titanium oxide, zirconium oxide and thorium oxide at 2300 - 2400°C have been investigated (ref. 4). It was shown that at high temperature the ZrC-ThO<sub>2</sub>, TiC-ThO<sub>2</sub>, ZrC-ZrO<sub>2</sub>, TiC-ZrO<sub>2</sub> systems complex oxidation-reduction processes take place in a vacuum, associated with changes of the composition and the volume of the crystal lattices of the starting components. These cermets were quite strong, had a high melting point and had increased stability to the various corrosive media.

For further investigations in this field the authors of this article chose such compositions in which the most easily available refractory oxide ZrO<sub>2</sub> is combined with carbides of titanium, niobium and zirconium. Some of the information on the starting materials is given in Table 1.

For the investigation we prepared pressed pellets from the appropriate mixtures which were sintered at  $10^{-3}$  -  $10^{-4}$  mm pressure at different temperatures and for different durations of time. The samples contain from 5-10 to 90 - 95 percent of each of the components.

We investigated the properties of samples from these mixtures in the ZrC-ZrO<sub>2</sub> system of different raw material compositions: 10 - 50 percent ZrC and 90 - 50 percent ZrO<sub>2</sub> (Tables 2 - 4). The specimens in the ZrC-ZrO<sub>2</sub> system

Table 1

## CHARACTERISTIC OF STARTING MATERIAL

Material	Lattice Constant kX	Bound Carbon Content, %	Conditions of Production	Crystal Lattice
ZrC	4.6705	11.29	- -	Cubic of NaCl type
NbC	4.4600	11.24	- -	the same
TiC	4.3171	18.20	- -	the same
ZrO <sub>2</sub>	5.109	- -	Pure, stabilized with 6 wt. % of CaO at 1500°C	Cubic of CaF <sub>2</sub> type
ZrO <sub>2</sub>	5.075	- -	Pure, stabilized by fusion	the same
ZrO <sub>2</sub>	- -	- -	Pure, unstabilized	Monoclinic

Table 2

PROPERTIES OF CERMETS FROM A MIXTURE OF ZrC-ZrO<sub>2</sub> (monoclinic)

Composition, wt. %		Sintering Temperature °C	Weight Loss %	Volume Shrinkage %	Porosity %	Specific Density g/cm <sup>3</sup>	Yield Point During Compression 10 <sup>-2</sup> kg/cm <sup>2</sup>	Shear Modulus G·10 <sup>-5</sup> kg/cm <sup>2</sup>	Electrical Destruction mm <sup>3</sup> /min
ZrO <sub>2</sub>	ZrC								
100	- -	2400	0.39	10.7	18.5	4.75	4.67	- -	- -
95	5	2400	4.30	14.5	11.9	4.91	4.97	5.29	0.200
90	10	2300	5.40	25.4	0.5	5.73	32.50	8.76	0.658
50	50	2300	+0.50	13.2	15.0	5.37	10.02	4.51	1.300
10	90	2300	+0.46	1.7	27.8	4.76	2.51	- -	9.000
- -	100	2400	0.35	1.4	36.1	4.23	5.31 <sup>1</sup>	- -	2.434

<sup>1</sup>The bending strength  $\sigma_{\text{bend}} \cdot 10^{-2}$ , kg/cm<sup>2</sup>.

(stabilized with 6 percent CaO) had the greatest density and were the strongest when the content of ZrC was 10 percent. The specimens from mixtures in the ZrC-ZrO<sub>2</sub> system (fuzed) were the strongest when the content of ZrC was 50 percent.

Table 3

PROPERTIES OF CERMETS FROM A MIXTURE OF ZrC-ZrO<sub>2</sub> (Stabilized with 6 % CaO)

Composition, wt. %		Sintering Temperature °C	Weight Loss %	Volume Shrinkage %	Porosity %	Specific Density g/cm <sup>3</sup>	Yield Point During Com- pression $\sigma \cdot 10^{-2}$ kg/cm <sup>2</sup>	Shear Modulus $G \cdot 10^{-5}$ kg/cm <sup>2</sup>	Electrical Destruction mm <sup>3</sup> /min
ZrO <sub>2</sub>	ZrC								
100	- -	2300	1.0	12.7	9.50	4.87	7.70	7.50	- -
90	10	2300	7.6	12.4	20.50	4.87	10.26	- -	0.468
50	50	2300	9.6	10.1	32.40	4.51	7.55	2.393	1.011
10	90	2300	5.9	2.3	41.03	4.07	2.60	- -	8.030
- -	100	2300	0.35	1.4	36.10	4.23	5.28 <sup>1</sup>	- -	2.500

<sup>1</sup> The bending strength  $\sigma_{\text{bend}} \cdot 10^{-2}$ , kg/cm<sup>2</sup>.

Table 4

PROPERTIES OF CERMETS FROM A MIXTURE OF ZrC-ZrO<sub>2</sub> (Stabilized<sup>by</sup> fusion)

Composition, wt. %		Sintering Temperature °C	Weight Loss %	Volume Shrinkage %	Porosity %	Specific Density g/cm <sup>3</sup>	Yield Point During Com- pression $\sigma \cdot 10^{-2}$ kg/cm <sup>2</sup>	Shear Modulus $G \cdot 10^{-5}$ kg/cm <sup>2</sup>	Electrical Destruction mm <sup>3</sup> /min
ZrO <sub>2</sub>	ZrC								
100	- -	2300	7.5	11.6	10.3	5.15	12.00	5.000	- -
90	10	2300	12.5	7.1	19.7	4.41	12.30	3.400	0.175
80	20	2300	8.5	12.5	8.1	5.00	22.30	5.264	0.454
50	50	2400	8.9	14.2	10.3	5.64	26.76	5.330	1.329
30	70	2400	13.8	12.5	39.5	5.01	16.90	4.500	2.874
10	90	2300	4.9	1.4	40.4	4.17	2.60	2.000	7.395
- -	100	2300	0.4	1.4	36.1	4.20	5.28 <sup>1</sup>	- -	2.500

<sup>1</sup> The bending strength  $\sigma_{\text{bend}} \cdot 10^{-2}$ , kg/cm<sup>2</sup>.

The greatest loss in weight by specimens occurs in cermets containing  $\text{ZrO}_2$  stabilized by fusion, i.e., that in which the stabilization process has been carried out to the greatest extent of completion.<sup>1</sup>

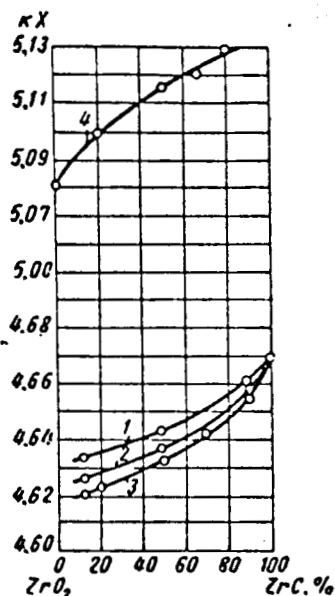


Figure 1. Lattice periods as a function of  $\text{ZrO}_2$  and  $\text{ZrC}$  content in the cermet sintered at  $2300^\circ\text{C}$ .  $\text{ZrC}$  lattice with: 1 -  $\text{ZrO}_2$  monoclinic; 2 -  $\text{ZrO}_2$  cubic stabilized with 6 percent  $\text{CaO}$ ; 3 -  $\text{ZrO}_2$  cubic stabilized by fusion; 4 - cubic lattice of  $\text{ZrO}_2$ .

<sup>1</sup>The X-ray diffraction pattern of cubic  $\text{ZrO}_2$  shows the last pronounced lines at an angle  $73.1^\circ \theta$ .

The X-ray investigations (fig. 1) show that decrease of the lattice parameter of zirconium carbide is more intense with fusion stabilized  $\text{ZrO}_2$  and the least pronounced for monoclinic  $\text{ZrO}_2$ .

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The results show that the greatest interaction of  $\text{ZrC}$  occurs with cubic zirconium dioxide which was stabilized by fusion. The interaction of  $\text{ZrC}$  with  $\text{ZrO}_2$  stabilized with 6 percent  $\text{CaO}$  at  $1500^\circ\text{C}$ , is intermediate in terms of intensity between the fused and the monoclinic  $\text{ZrO}_2$ . This is apparently associated with the fact that <sup>6%</sup><sub>4</sub>  $\text{CaO}$  stabilized zirconium dioxide contained a significant amount of monoclinic  $\text{ZrO}_2$ .<sup>1</sup>

It is also apparent from figure 1 that during the increase of the concentration of zirconium carbide in cermet. The zirconium dioxide lattice expands. This can be explained by the increased oxygen deficiency in  $\text{ZrO}_2$  as the concentration of zirconium carbide is increased since in the  $\text{ZrO}_2$  lattice repulsion increases between the positively charged zirconium ions in places where oxygen is deficient.

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The monotonic decrease of the intensity of the change of the lattice parameters of the components in the  $\text{ZrC-ZrO}_2$  and the  $\text{TiC-ZrO}_2$  systems (fig. 2) supports the previously made conclusion (ref. 4) regarding the gradual decrease of the interaction in systems of various refractory oxides and carbides up to  $2400^\circ\text{C}$ . This may serve as an indication of the stability of such cermets at sufficiently high temperatures. The formation of the oxycarbide type of compounds which were reported in reference 3 were not verified by us through X-ray defraction.

<sup>1</sup>On the X-ray diffraction pattern the last lines for cubic  $\text{ZrO}_2$  were observed at  $55.1^\circ \theta$  and also weak lines for monoclinic  $\text{ZrO}_2$  were observed at  $14.3$  and  $15.9^\circ \theta$ .

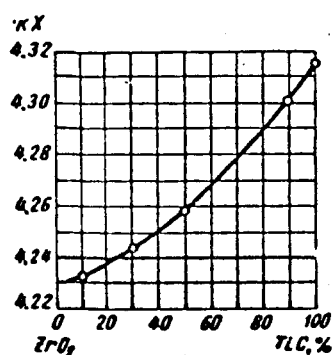


Figure 2. Change of the lattice period of TiC as a function of  $ZrO_2$  content in the cermet made of a TiC- $ZrO_2$  mixture.

The properties of cermets prepared from mixtures of TiC and  $ZrO_2$  are shown in Table 5. It is indicated, by the weight loss and the changes of the lattice parameters of TiC as a function of the content of  $ZrO_2$  in a cermet, that interaction between TiC and  $ZrO_2$  is more intense than in cermets prepared from ZrC- $ZrO_2$  mixtures. This apparently is associated with the fact that the homogeneity region of TiC is broader than that of ZrC.

Table 5

PROPERTIES OF CERMETS FROM A MIXTURE OF TiC- $ZrO_2$  (monoclinic)

Composition, wt. %		Sintering Temperature °C	Weight Loss %	Volume Shrinkage %	Porosity %	Specific Density g/cm <sup>3</sup>	Yield Point During Compression $10^{-2}$ kg/cm <sup>2</sup>	MShear Modulus $G \cdot 10^{-5}$ kg/cm <sup>2</sup>	Electrical Destruction mm <sup>3</sup> /min
ZrO <sub>2</sub>	ZrC								
100	- -	2300	0.39	10.7	18.50	4.75	4.68	5.00	- -
90	10	2300	9.67	24.14	3.12	5.86	17.22	6.33	0.701
50	50	2400	17.27	16.9	19.32	4.55	4.3	- -	1.67
10	90	2400	31.59	22.31	1.05	5.70	7.6	3.22	1.78
- -	100	2300	3.7	9.3	8.09	4.37	22.5 <sup>1</sup>	- -	2.906

<sup>1</sup>The bending strength  $\sigma_{bend} \cdot 10^{-2}$ , kg/cm<sup>2</sup>



However, just as in mixtures of ZrC and  $\text{ZrO}_2$ , oxidation-reduction processes during temperature interaction of TiC with  $\text{ZrO}_2$  do not lead to the complete disappearance of the starting components (certainly when the content exceeds 10 percent).

The electrical destruction of cermets made of TiC and  $\text{ZrO}_2$  mixtures increases with increased content of TiC which apparently, just as in ZrC and  $\text{ZrO}_2$  mixtures, is associated <sup>with</sup> the overall increase of the electrical conductivity of the material. It is significant that when the content of  $\text{ZrO}_2$  in cermets is 5 - 10 percent the electrical destruction (see Tables 2-5) is significantly less than for a number of other materials (ref. 5).

Figure 3 shows the kinetic curves of the change of the content of carbon in carbide-oxide mixture; in the course of sintering the cermet at different temperatures the components were taken in equimolar ratios. The interaction of carbides with  $\text{ZrO}_2$  proceeds most intensely in the initial moments and decreases with time. During the increase of temperature the intensity of the reaction increases but the duration of the intense period decreases. Such an interaction can proceed when the reaction product is formed from the reacting substances which hinders the further interaction (fig. 4).

The reaction kinetics of the investigated carbides with zirconium dioxide cannot be described by equations of the first, second or third order. Consequently, despite the broadly accepted opinion, the rate of reaction in the solid phase is not always determined by the rate of diffusion of reagents as being the slowest stage of the process.

Figure 4 shows a microphotograph of sintered carbide-oxide cermets. At the boundaries of the carbide and oxide grains a third phase is formed. The coefficient of reflection of this phase is higher than the coefficient of

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reflection of carbide and thus it must be higher than that of oxide. Its microhardness is  $\sim 150-550 \text{ kg/mm}^2$ , i.e., it is very close to the microhardness of metal. This figure may be too high because the amount of this phase is very small. It was not possible to compare this phase chemically or by X-ray diffraction with any of the well-known substances, and during the determination of the microhardness it was necessary to work with loads applied to the indenter, which were much less than the optimum required for its performance.

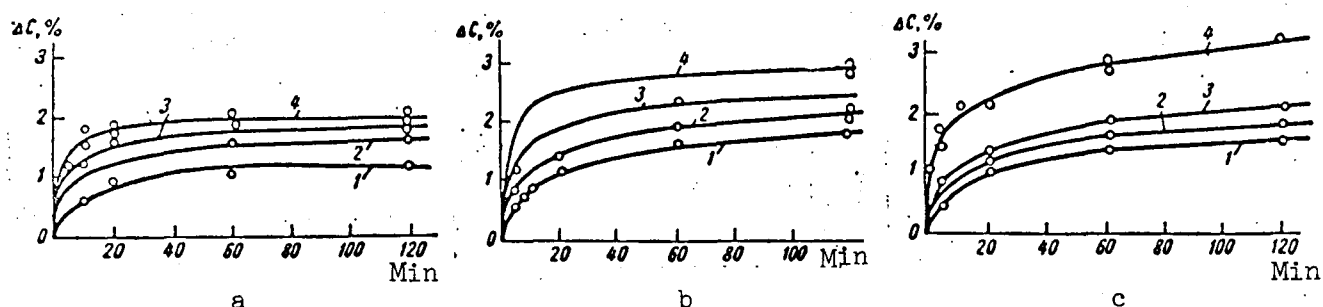


Figure 3. Change of the content of bound carbon in oxide-carbide cermets during heating ( $\Delta C$  is the difference between the initial and the final content of carbon in the sample). a -  $\text{ZrC} - \text{ZrO}_2$ ; b -  $\text{TiC} - \text{ZrO}_2$ ; c -  $\text{NbC} - \text{ZrO}_2$ ; 1 -  $1400^\circ\text{C}$ ; 2 -  $1600^\circ\text{C}$ ; 3 -  $1800^\circ\text{C}$ ; 4 -  $2000^\circ\text{C}$ .

In addition the grains of the third phase were surrounded by grains of zirconium carbide and zirconium dioxide, the microhardness of which was  $2500 - 3200$  and  $100 - 1250 \text{ kg/mm}^2$  respectively. This apparently resulted in the significant scattering of the obtained values for the microhardness of the third phase. In the  $\text{ZrC}-\text{ZrO}_2$  system the third phase can be compared with metallic zirconium which contains a certain amount of dissolved carbon, oxygen and nitrogen. It is less probable to compare this phase with oxycarbide as it was observed in the  $\text{Al}_2\text{O}_3-\text{C}$  system (ref. 6), since oxycarbide should be much closer to carbide and oxide in microhardness than to metal.

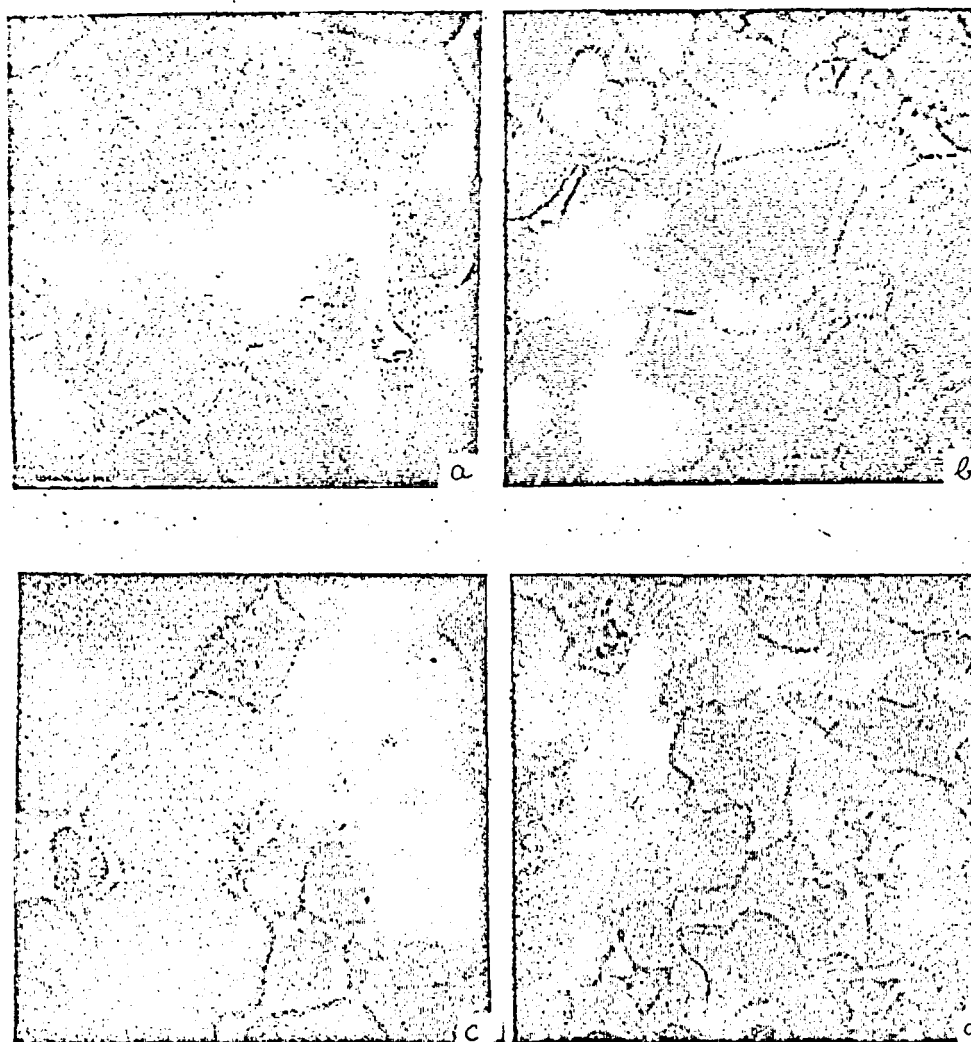


Figure 4. Micro structure of oxide-carbide cermets after sintering at 2300 - 2400°C. <sup>percent ZrO<sub>2</sub> and 80</sup> a - 20<sub>4</sub> percent ZrC; b - 50 percent ZrO<sub>2</sub> and 50 percent ZrC; c - 90 percent ZrO<sub>2</sub> and 10 percent ZrC; d - 50 percent TiC and 50 percent ZrO<sub>2</sub>, x 1350.

The greatest microhardness of carbide and oxide grains is in the middle of the grain. Figure 4b clearly shows that carbide and oxide grains are surrounded by the reaction zone. This zone is relatively shallow (apparently less than 0.5  $\mu$ ) thus it was not possible to determine its nature, properties and

structure. Prolonged sintering does not produce any significant increase in the depth of this zone as indicated in figure 3a, b and c.

The presented data may be used to a certain extent as the proof of the stability of properties of oxycarbide cermets, especially from mixtures of ZrC with  $ZrO_2$ . This indicates the possibility of using such cermets in high temperature technology.

However, upon increase of the deficiency of carbon the melting point of carbide lowers along the solidus line of the Me-C phase diagram. Therefore, in order to evaluate the durability of such a cermet in practical use at high temperatures it is necessary to take into account the gradual decrease of its melting point. Thus, <sup>by</sup>extrapolation of the kinetic curves of figure 3 to 100 hours at 2000°C and using the appropriate phase diagrams (refs. 7-9), it is possible to show that the melting point of the carbide phase in the ZrC- $ZrO_2$  system will be lowered to 3000°C, TiC- $ZrO_2$  -- to 2300°C and NbC- $ZrO_2$  -- to 2800°C.

The greatest lowering of the melting phase due to the great loss of carbon is observed in the cermet from the mixture of TiC and  $ZrO_2$ , despite the fact that the rate of reaction between NbC and  $ZrO_2$  at the same temperature and the same duration of sintering is greater than between TiC and  $ZrO_2$ . Therefore, in terms of stability of properties one should prefer cermets made from mixtures of TiC- $ZrO_2$  and ZrC- $ZrO_2$ .

#### Conclusions

Cermets made of ZrC and  $ZrO_2$  mixtures are the most stable at high temperatures. Cermets made from TiC and  $ZrO_2$  and also NbC and  $ZrO_2$  mixtures are somewhat less stable. A third phase was established as the reaction product in

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oxide-carbide cermets. The properties of this phase are close to the elemental metal, but due to the small amount of this phase it was not possible to compare it with known substances.

The decrease of lattice parameters of carbide with increase of the concentration of zirconium dioxide is gradually decreased. The zirconium dioxide lattice is somewhat expanded when the content of carbide in the cermet is increased. Zirconium dioxide stabilized by fusion has the greatest effect on the decrease of lattice parameters of zirconium carbide. Monoclinic zirconium dioxide has the smallest effect.

The properties of cermets made of mixtures of  $ZrC$  and  $ZrO_2$  and also  $TiC$  and  $ZrO_2$  indicate the possibility of their use as structural materials for high temperature work.

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